

US 5558959  
WO 9603781A1

INTERNATIONAL APPLICATION PUBLISHED UN

(51) International Patent Classification<sup>6</sup> :

H01M 6/18, 10/40

A1

(11) International Publication Number:

WO 96/03781

(43) International Publication Date:

8 February 1996 (08.02.96)

(21) International Application Number: PCT/US95/09117

(22) International Filing Date: 19 July 1995 (19.07.95)

(30) Priority Data:

08/279,131

22 July 1994 (22.07.94)

US

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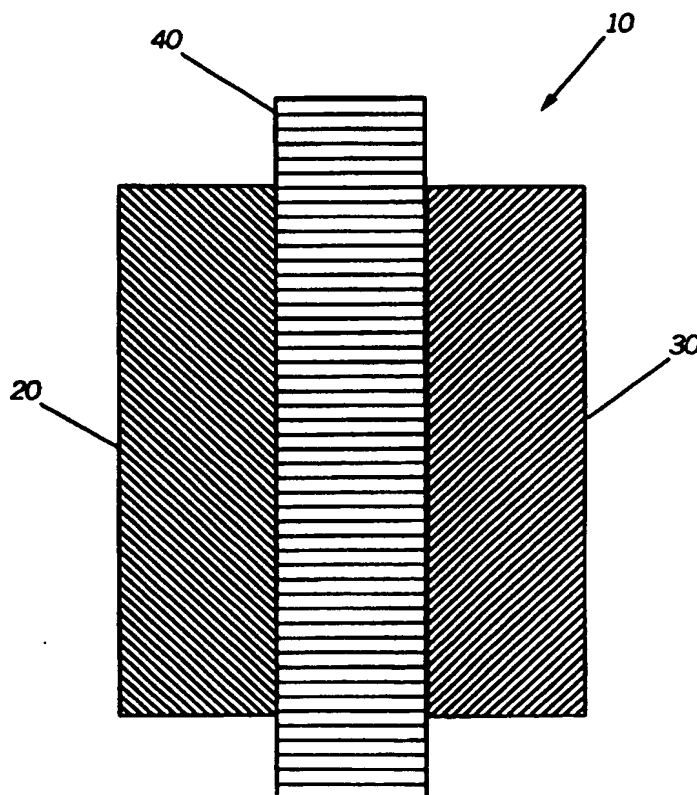
(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG).

**Published***With international search report.**Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.*

(54) Title: POLYURETHANE BASED ELECTROLYTES FOR ELECTROCHEMICAL CELLS AND ELECTROCHEMICAL CELLS USING SAME

## (57) Abstract

An electrolyte system (40) for use in connection with an electrochemical cell (10). The cell (10) includes a positive (20) and a negative (30) electrode and the electrolyte system (40) disposed therebetween. The electrolyte system includes a liquid electrolyte adapted to provide ion transport between the positive and negative electrodes and a segmented block copolymeric support structure for engaging the liquid electrolyte.



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**POLYURETHANE BASED ELECTROLYTES FOR  
ELECTROCHEMICAL CELLS AND ELECTROCHEMICAL CELLS  
USING SAME**

**5    Technical    Field**

          This invention relates in general to electrolytes for electrochemical cells, and more particularly to polymer electrolytes for such cells.

**10   Background    of    the    Invention**

          There has been a great deal of interest in developing better and more efficient methods for storing energy for applications such as radio communication, satellites, portable computers and electric vehicles to name but a few. There have also been concerted efforts  
15    to develop high energy, cost effective batteries having improved performance characteristics, particularly as compared to storage systems known in the art.

          Rechargeable, or secondary cells are more desirable than primary (non-rechargeable) cells since the associated chemical  
20    reactions which take place at the positive and negative electrodes of the battery are reversible. Electrodes for secondary cells are capable of being regenerated (i.e. recharged) many times by the application of an electrical charge thereto. Numerous advanced electrode systems have been developed for storing electrical charge.  
25    Concurrently, much effort has been dedicated to the development of electrolytes capable of enhancing the capabilities of electrochemical cells.

          Heretofore, electrolytes have been either liquid electrolytes as are found in conventional wet cell batteries, or solid films as are  
30    available in newer, more advanced battery systems. Each of these systems have inherent limitations, and related deficiencies which make them unsuitable for various applications.

          Liquid electrolytes, while demonstrating acceptable ionic conductivity, tend to leak out of the cells into which they are sealed.  
35    While better manufacturing techniques have lessened the occurrence of leakage, cells still do leak potentially dangerous liquid

electrolytes from time to time. This is particularly true of current lithium ion cells. Moreover, any leakage from the cell lessens the amount of electrolyte available in the cell, thus reducing the effectiveness of the cell. Cells using liquid electrolytes are also not available for all sizes and shapes of batteries.

Conversely, solid electrolytes are free from problems of leakage. However, they have vastly inferior properties as compared to liquid electrolytes. For example, conventional solid electrolytes have ionic conductivities in the range of  $10^{-5}$  S/cm, whereas acceptable ionic conductivity is  $> 10^{-3}$  S/cm. Good ionic conductivity is necessary to ensure a battery system capable of delivering usable amounts of power for a given application. Good conductivity is necessary for the high rate operation demanded by, for example, cellular telephones and satellites. Accordingly, solid electrolytes are not adequate for many high performance battery systems.

Examples of solid polymer electrolytes, include dry solid polymer systems in which a polymer, such as polyurethane, is mixed with an electrolyte salt in dry or powdered form. These types of systems are disclosed in, for example, *Ionic Conductivity of Polyether-Polyurethane Networks Containing Alkali Metal Salts. An Analysis of the Concentration Effect*, Macromolecules, Vol. 17, No. 1, 1984, pgs. 63-66, to Killis, et al; and *Poly(dimethylsiloxane) - Poly(ethylene oxide) Based Polyurethane Networks Used As Electrolytes in Lithium Electrochemical Solid State Batteries*, Solid State Ionics, 15 (1985) 233-240, to Bouridah, et al.. Unfortunately, these dry systems, like the solid electrolytes discussed above, are characterized by relatively poor ionic conductivity.

One solution which has been proposed relates to the use of so-called gel electrolytes for electrochemical systems. Gels, or plasticized polymeric systems are wet systems, not dry, as described above. Heretofore most gel electrolyte systems have been based on homopolymers, i.e, single polymer systems. Homopolymer-based gel electrolytes have not been successful as they tend to dissolve in higher concentrations of the electrolyte solvent, thus losing mechanical integrity.

Accordingly, there exists a need for a new electrolyte system which combines the mechanical stability and freedom from leakage offered by solid electrolytes with the high ionic conductivities of liquid electrolytes.

### Brief Description of the Drawings

FIG. 1 is a schematic representative of an electrochemical cell in accordance with the instant invention;

FIG. 2 is a schematic morphology of unstretched segmented block polyurethane copolymers in accordance with the instant invention;

FIG. 3 is an AC impedance spectrum of a polyurethane/liquid electrolyte system in accordance with the instant invention;

FIG. 4 is a cyclic voltammagram of a polyurethane/liquid electrolyte blend, and

FIG. 5 is an chart illustrating the conductivity of solvent-cast polyurethane/liquid electrolyte blends as a function of electrolyte composition.

### Detailed Description of the Preferred Embodiment

While the specification concludes with claims defining the features of the invention that are regarded as novel, it is believed that the invention will be better understood from a consideration of the following description in conjunction with the drawing figures, in which like reference numerals are carried forward.

Referring now to FIG. 1, there is illustrated therein a schematic representation of an electrochemical cell in accordance with the instant invention. The cell (10) includes a positive electrode (20) and a negative electrode (30). The positive electrode (20) may be fabricated of any of a number of chemical systems known to those of ordinary skill in the art. Examples of such systems include, but are not limited to, manganese oxide, nickel oxide, cobalt oxide, vanadium oxide, and combinations thereof. The negative electrode (30) may likewise be fabricated from any of a number of electrode materials known to those of ordinary skill in the art. Selection of the negative electrode material is dependent on the selection of the positive electrode so as to assure an electrochemical cell which will function properly for a given application. Accordingly, the negative electrode may be fabricated from, for example, alkali metals, alkali metal alloys, carbon, graphite, petroleum coke, and combinations thereof.

Operatively, disposed between the positive (20) and negative (30) electrodes is an electrolyte system (40). The electrolyte system (40) comprises an organic polymeric support structure adapted to engage, as for example, by absorption, an

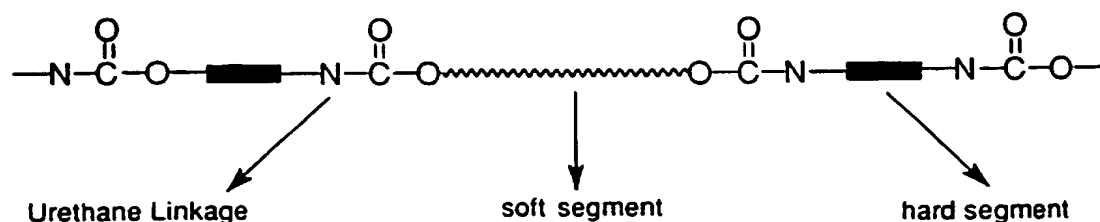
5 electrochemically active species or material. The electrochemically active material may be a liquid electrolyte, such as a metal salt that is dissolved in an organic solvent and which is adapted to promote ion transport between said positive (20) and negative (30) electrodes.

10 The liquid electrolyte absorbed by the organic support structure is selected to optimize performance of the positive (20) and negative (30) electrode couple. Therefore, in an embodiment for a lithium based electrochemical cell, the liquid electrolyte absorbed by the organic support structure is typically a solution of  
15 an alkali metal salt, or combination of salts, dissolved in an aprotic organic solvent or solvents. Typical alkali metal salts include, but are not limited to, salts having the formula  $M^+X^-$  where  $M^+$  is a alkali metal cation such as  $Li^+$ ,  $Na^+$ ,  $K^+$  and combinations thereof; and  $X^-$  is an anion such as  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $ClO_4^-$ ,  $BF_4^-$ ,  $PF_6^-$ ,  $AsF_6^-$ ,  
20  $SbF_6^-$ ,  $CH_3CO_2^-$ ,  $CF_3SO_3^-$ ,  $(CF_3O)_2N^-$ ,  $(CF_3SO_2)_2N^-$ ,  $(CF_3SO_2)_3C^-$ , and combinations thereof. Aprotic organic solvents include, but are not limited to, propylene carbonate, ethylene carbonate, diethyl carbonate, dimethyl carbonate, dipropyl carbonate, dimethyl sulfoxide, acetonitrile, dimethoxyethane, diethoxyethane,  
25 tetrahydrofuran, and combinations thereof.

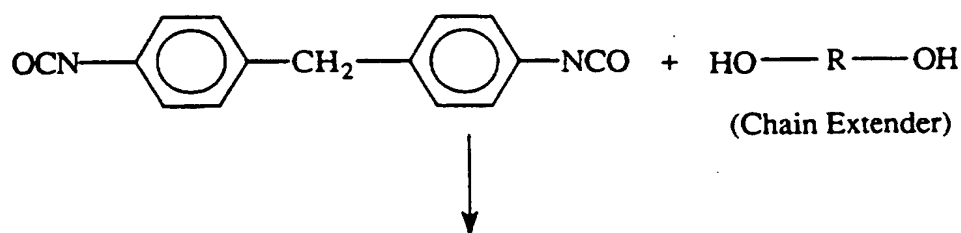
The organic polymeric support structure may be fabricated of a segmented block copolymer, that is a polymer that has at least two different blocks that form alternating segments along the polymer chain, each segment having different physical properties. An  
30 example of a segment block copolymer as used in the instant invention is the polyurethane thermoplastic elastomer which is a copolymer of a short-chain diisocyanate and a dihydroxy-terminated polyester (polyester diol). The condensation of these two species leads to the formation of a polymer having urethane linkages as  
35 illustrated in greater detail below.

The segmented block copolymer material from which the organic polymeric support structure is fabricated may be depicted as follows:

5 The segmented block copolymer material from which the organic polymeric support structure is fabricated may be depicted as follows:



10 The short-chain diisocyanates form the hard-rigid block segments of the copolymer. The short-chain diisocyanates are typically condensation products of diphenyl methane diisocyanate (MDI) and small molecule diols, for example, butane diol or ethylene glycol, or small molecular diamines such as 4-4'-methylene bis (2-chloroaniline).  
 15 The short-chain diols/diamines are also referred to as chain-extenders. The condensation reaction leading to the formation of the diisocyanate-terminated hard block segments may be described as follows:



Diisocyanate Terminated Hard Segment

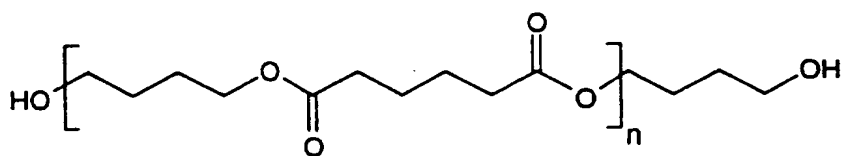
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The long chain diols provide the soft block segment of the copolymer, and are typically relatively high-molecular weight (<3500 g/M hydroxyl terminated polyesters or hydroxyl terminated  
 25 polyethers. In one preferred embodiment the polyester is a



polybutylene adipate (molecular weight approximately 2000 g/M). Alternatively, the polyester diols may be, for example, polyethylene adipate, polycaprolactone and combinations thereof. The long-chain diols forming the soft blocks typically appear as follows:

5



polybutylene adipate

The hard block segments are known to aggregate through hydrogen bonding thus behaving as physical crosslinks for the soft block segments. As a result the polymeric material is an elastomer, that is, a rubbery material. Further, the hydrogen bonds responsible for aggregation of the hard blocks may be broken at high temperatures allowing the materials to behave as a thermoplastic. This property of the polyurethane offers an immense processing advantage since it may be processed into sheets and films using conventional polymer processing equipment like those used for conventional thermoplastics at high temperatures while behaving like elastomers at lower temperatures.

Referring now to FIG. 2, there is illustrated therein the schematic morphology of an unstretched segmented block polyurethane copolymer in accordance with the instant invention. The copolymer (60) is characterized by two general types of polymeric segments; a plurality of bodies of hard block segments (62, 64, and 66) which behave as physical crosslinks or backbone of the polymeric material. Disposed around and between the bodies of hard block segments are the long flexible chain polyester diols forming the soft block segments (68) of the copolymeric material (60).

Exemplary materials which may be used as the segmented block copolymers for the organic polymeric support structure of the instant invention include a polyurethane, (either polyether or

polyester based), polyester-polyether systems, polycarbonate-polyether systems and combinations thereof. Examples of segmented polyurethanes include Miles Laboratories Texin™ 480A, 455A, and 360D polyester/polyurethane material. These materials are approximately 2000 molecular weight alcohol terminated aliphatic polyesters for example polyethylene or polybutylene adipates, condensed with a diisocyanate made from MDI and a chain extender, as discussed above. Other examples of polyester-polyurethanes include Estane 58206 and 58209 which are polyurethanes formed by the MDI-containing diisocyanates with alcohol terminated polyesters such as polyethylene and/or polybutylene adipates, polycaprolactone or polyesters containing aromatic moieties. Similar polyester based polyurethanes are also available from Dow Corporation under the name Pellethane™ 2355-78A and 2102-75A.

Heretofore, most blends of electrochemically active materials such as electrolytes and polymers other than polyurethane resulted in a significant deterioration of the mechanical properties of the polymer, usually forming tacky, viscous fluids. Further, prior art combinations of polymers with electrolytes resulted in electrolytic behavior considerably lower than that considered acceptable in most electrochemical systems. Accordingly, an electrolyte in accordance with the instant invention has ionic conductivity as high as  $10^{-3}$  S/cm at room temperature, and has demonstrated excellent mechanical properties such as a shear modulus of approximately  $1 \times 10^5$  Pa at 30°C. Moreover, being elastomeric thermoplastics, these materials may form intimate contact with positive (20) and negative (30) electrodes.

More particularly, a polyurethane/liquid electrolyte system (40) in accordance with the instant invention may be mixed with cathode powders such as lithium manganese oxide, lithium nickel oxide or lithium cobalt oxide to form composite cathodes. Cathodes made in this fashion are essential for batteries which use polymer-based electrolytes since intimate contact between the active electrolyte material and the cathode cannot otherwise be achieved. It may further be appreciated that polyurethane liquid electrolyte

blends in accordance with the instant invention may also be used to form composite anodes and batteries where lithium cannot be used.

5       The instant electrolyte system also has the important advantage of having a polymeric support structure which is easily processable and reprocessable, since the materials are thermoplastic elastomers. Other prior art gel systems are typically permanently chemically cross-linked either by radiation (e-beam, UV, etc.) or by using a chemical crosslinking agent, for example, diisocyanates which can be used to cross-link polyether triols.

10       The following examples are intended to illustrate the advantages of the instant invention and they are not intended to be limitations thereof.

### EXAMPLE I

A polyurethane based electrolyte system in accordance with the instant invention was made by the solvent casting technique. 0.5 grams of Miles Texin 480A, polyester/polyurethane and 2.0g of a 1M solution of lithium tetrafluoroborate ( $\text{LiF}_4$ ) solution in propylene carbonate were dissolved in approximately 8g of tetrahydrofuran (THF). This solution was poured into an aluminum dish and the THF was allowed to evaporate overnight yielding a film of the polyurethane based electrolyte. The resulting electrolyte system was comprised of approximately 80 wt% of the liquid electrolyte (propylene carbonate/ $\text{LiBF}_4$ ). Samples measuring approximately  $1 \text{ cm}^2$  in area were prepared from the solvent cast film.

Referring now to FIG. 3, there is illustrated therein the AC impedance spectrum of polyurethane blended with 80% (by weight) of 1M solution of lithium tetrafluoroborate and propylene carbonate as described above. The resistance of the film was approximately 55 Ohms. The thickness of the sample was approximately 0.075 cm with a cross-sectional area of approximately  $1 \text{ cm}^2$ . Based upon this and as illustrated by the series of points shown in FIG. 3, the conductivity of the film was calculated to be approximately  $1.4 \times 10^{-3} \text{ s/cm}$ .

### EXAMPLE II

A second polyurethane based electrolyte was made by the solvent casting technique as follows. 0.5 grams of a Miles Texin™ 480A polyester polyurethane and 0.8 grams of 1M solution of  $\text{LiBF}_4$  solution in propylene carbonate (PC) were dissolved in about 8 grams of THF. The solution was poured in an aluminum dish and the THF was allowed to evaporate overnight yielding a film of the polyurethane based electrolyte. The resulting electrolyte comprised 62 wt% of the liquid electrolyte (PC- $\text{LiBF}_4$ ). Samples (approximately  $1 \text{ cm}^2$  in area and 0.036 cm thick) for conductivity measurements were cut out from this solvent cast film. The resistance of the film was 130 Ohms and the conductivity was calculated to be  $3 \times 10^{-4} \text{ S/cm}$ .

Referring now to FIG. 4, there is illustrated therein a cyclic voltammagram for the material obtained as described above. Data was collected at a scan rate of approximately 1 mV/s with platinum mesh working and counter electrodes, and a lithium reference electrode.

Cyclic voltammetry studies of the polyurethane electrolyte indicated that the material has good electrochemical stability in the voltage range between 0.2 and 4.2 V. The steep increase at around 4.2V indicates that the electrolyte is beginning to oxidize at this voltage. The source of the two peaks in the range 1 to 3.5V is not known and may be attributed to impurities in the polyurethane based electrolyte system. However, it is important to note that the current(y-axis) scale of these peaks is only in the microamp range and hence the concentration of the electrochemically active species that is involved is quite small.

### EXAMPLE III

A third polyurethane based electrolyte was made by the solvent casting technique as follows: 0.5 grams of Miles Texin™ 480A polyester polyurethane and 4.5 grams of 1M solution of lithium tetrafluoroborate solution in propylene carbonate were dissolved in about 8 grams of THF. The solution was poured in an aluminum dish and the THF was allowed to evaporate overnight yielding a film of the polyurethane based electrolyte. The resulting electrolyte comprised 90 wt% of the liquid electrolyte (PC-LiBF<sub>4</sub>). Samples (approximately 1cm<sup>2</sup> in area and 0.097 cm thick) for conductivity measurements were cut out from this solvent cast film. The resistance of the film was 47 ohms and the conductivity was calculated to be 3x10<sup>-3</sup>S/cm.

### EXAMPLE IV

Polyurethane gels may also be made without the use of casting solvents like THF, as follows: Polyurethane films, approximately 0.058 cm in thickness, were made by compression molding at around 170°C in a Carver press. These films were then soaked in 1M solution of lithium tetrafluoroborate solution in

propylene carbonate. After 48 hours the resulting polyurethane-liquid electrolyte blend contained about 63% of the liquid electrolyte. The sample thickness increased to 0.081 cm. Samples (approximately 1cm<sup>2</sup> in area) for conductivity measurements were cut out from this swollen film. The resistance of the film was 178 Ohms and the conductivity was calculated to be around 4.5x10<sup>-4</sup> S/cm.

Referring now to FIG. 5, there is illustrated therein a chart demonstrating the conductivity of solvent cast/polyurethane liquid electrolyte blends as a function of liquid electrolyte composition. In this regard, the conductivity of Example I is illustrated at Point 82 while the conductivity of Example II and III are illustrated by Points 84 and 86 respectively. As may be appreciated from a perusal of FIG. 5, numerous other samples having greater and lesser weight percents of liquid electrolyte in the solvent cast polyurethane material are illustrated. From this chart, one may conclude that with increasing wt.% of the liquid electrolyte material, conductivity similarly increases. Limitations to increased conductivity are derived principally from decreasing mechanical stability of the polyurethane support structure with increased concentrations of the liquid electrolyte. It is important to note, however, that wt.% as high as those illustrated in Point 86 demonstrate quite acceptable conductivity while retaining excellent mechanical properties.

While the preferred embodiments of the invention have been illustrated and described, it will be clear that the invention is not so limited. Numerous modifications, changes, variations, substitutions and equivalents will occur to those skilled in the art without departing from the spirit and scope of the present invention as defined by the appended claims.

What is claimed is:

**Claims**

1. An electrolyte system for use in electrochemical cell having positive and negative electrodes, said electrolyte system comprising:  
an electrochemically active liquid electrolyte material adapted  
5 to promote ion transport between said positive and negative electrodes; and  
a polymeric support structure fabricated of a segmented block copolymeric material, said segmented block copolymeric material adapted to absorb said electrochemically active material.  
10
2. An electrolyte system as in claim 1, wherein said polymeric support structure is a polyurethane-based polymeric support structure.
- 15 3. An electrolyte system as in claim 1, wherein said segmented block copolymeric materials comprises first and second block segments.
- 20 4. An electrolyte system as in claim 3, wherein said first segmented block comprises short-chain diisocyanates.
5. An electrolyte system as in claim 3, wherein said first segmented block comprises short-chain diisocyanates.
- 25 6. An electrolyte system as in claim 3, wherein said first segmented blocks is a soft block segment.
7. An electrolyte system as in claim 5, wherein said soft block segment is adapted to absorb said electrochemically active  
30 material.
8. An electrolyte system as in claim 7, wherein said soft-block segments are fabricated from hydroxyl terminated polyesters, hydroxyl terminated polyethers and combination thereof.  
35

9. An electrolyte system as in claim 1, wherein said liquid electrolyte is an alkali metal salt dissolved in an aprotic organic solvent.



10. An electrolyte system as in claim 7, wherein alkali metal salt is selected from the group consisting of materials having the  
5 formula  $M^+X^-$  where:

$M^+$  is an alkali metal cation such as  $Li^+$ ,  $Na^+$ , or  $K^+$ , and;

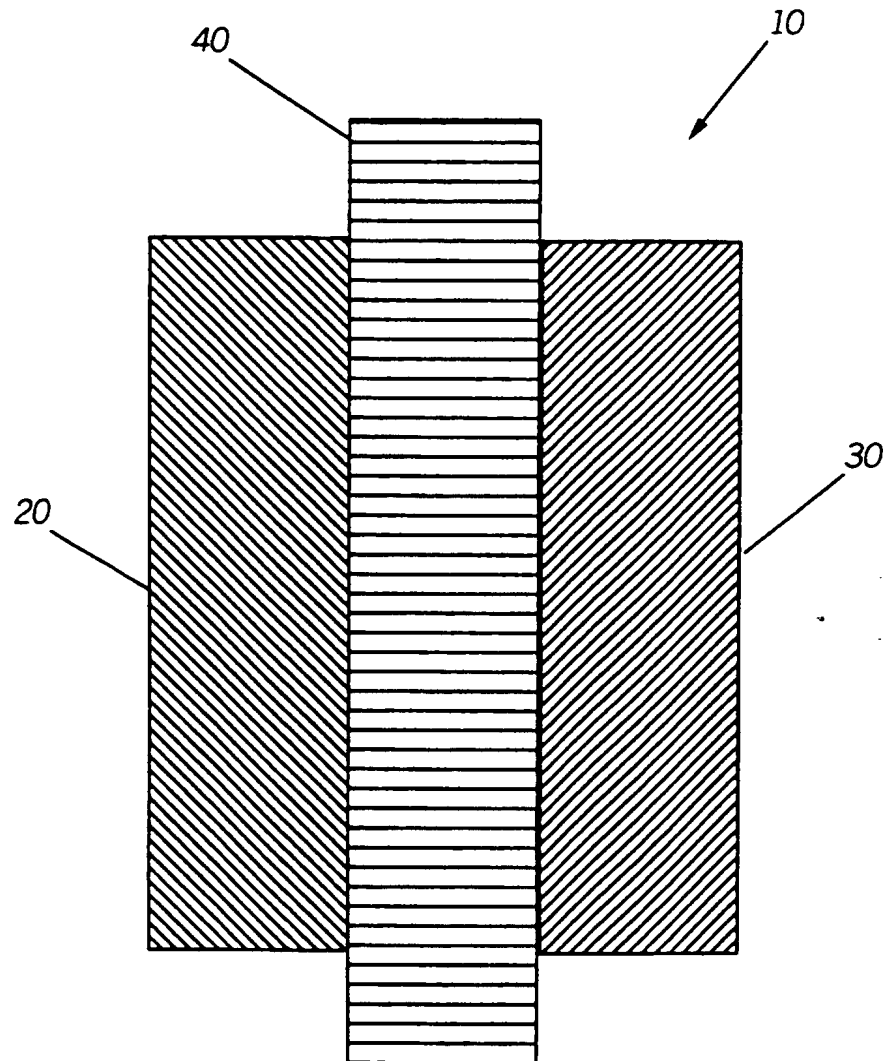
$X^-$  is an ion such as  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $ClO_4^-$ ,  $BF_4^-$ ,  $PF_5^-$ ,  $AsF_6^-$ ,  $SbF_6^-$ ,  $CH_3CO_2^-$ ,  $CF_3SO_3^-$ ,  $(CH_3CO_2)_2N^-$ ,  $(CF_3SO_2)_3C^-$ , and combinations thereof.

10

11. An electrolyte system as in claim 7, wherein said aprotic organic solvent is selected from the group consisting of propylene carbonate, ethylene carbonate, diethylcarbonate, dimethyl carbonate, dipropylcarbonate, dimethyl sulfoxide, acetonitrile,  
15 dimethyloxyethane, diethoxyethane, tetrahydrofuran and combinations thereof.

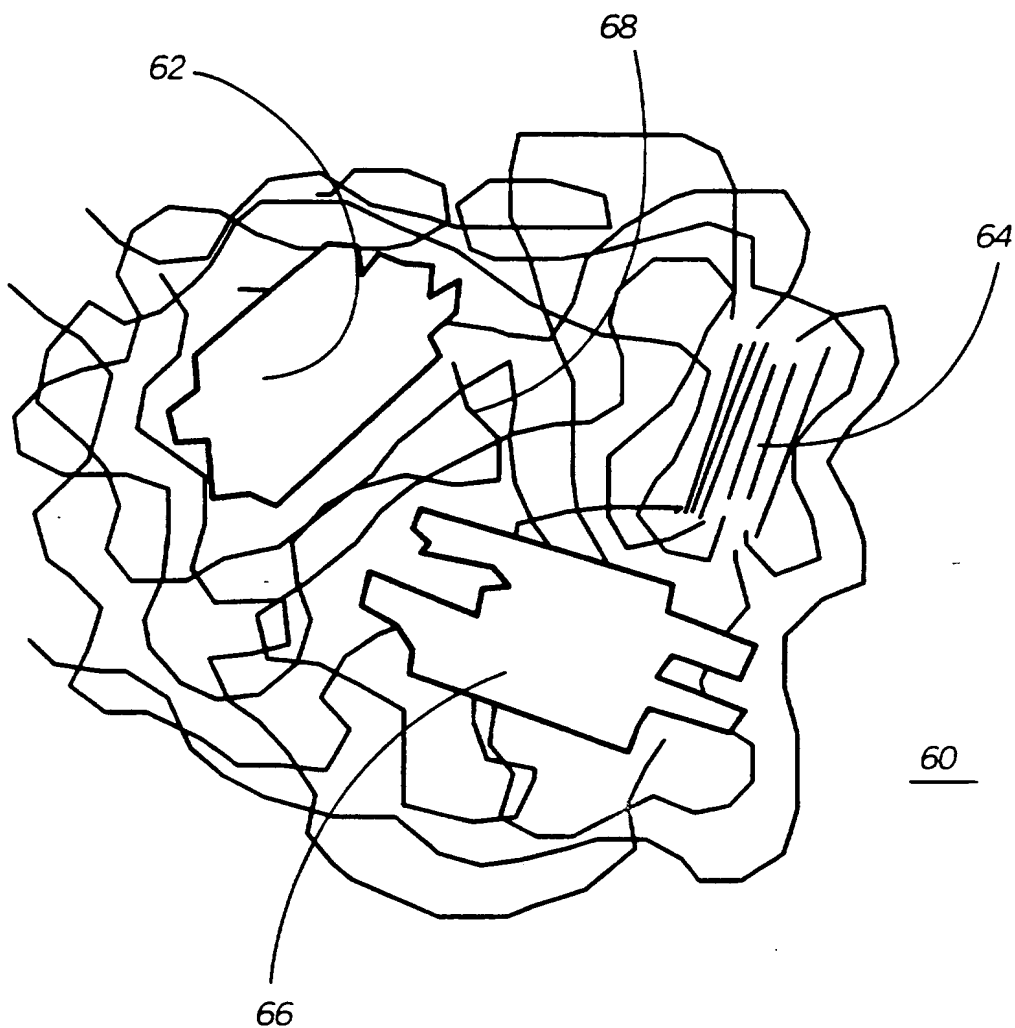
12. An electrolyte system as in claim 7 wherein said electrochemically active material is  $LiBF_4$  in propylene carbonate.

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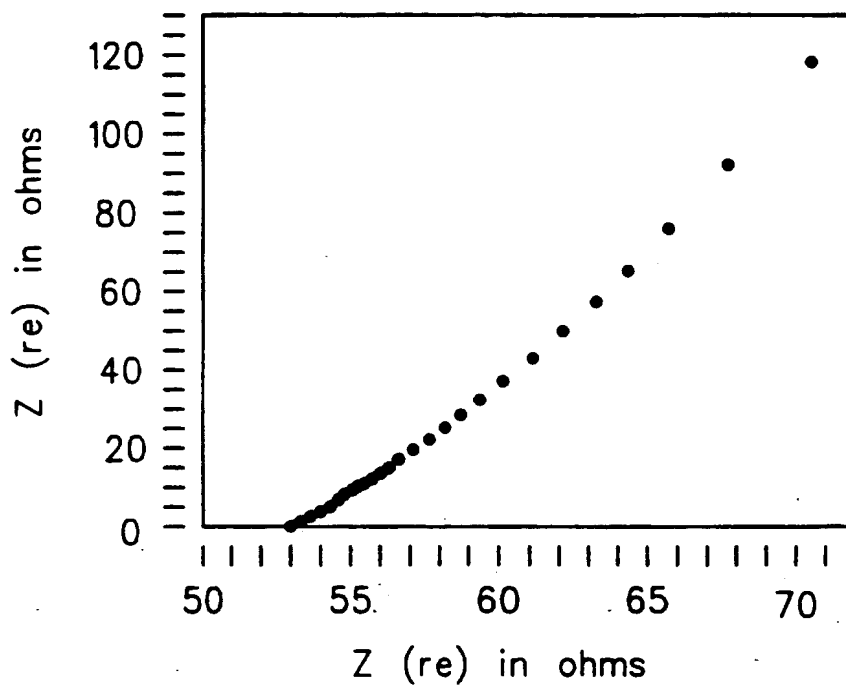
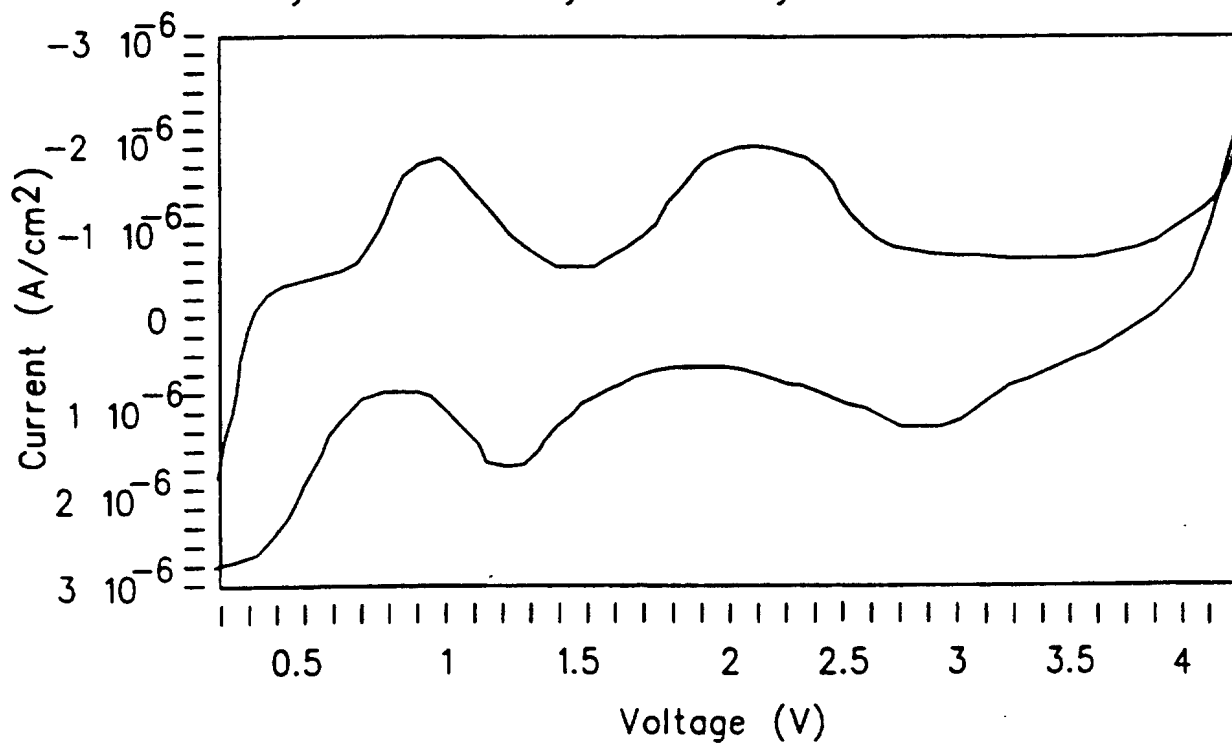
*FIG. 1*

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**FIG. 2**



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**FIG. 3**POLYURETHANE; LiBF<sub>4</sub>-PC (1M) (20;80) (t=750 microns)**FIG. 4**Cyclic Voltammetry Data: Polyurethane: PC-LiBF<sub>4</sub>

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US95/09117

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) : H01M 6/18, 10/40

US CL : 429/192; 252/62.2

According to International Patent Classification (IPC) r to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 429/188, 191, 192, 193; 252/62.2

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS: FILE USPAT

SEARCH TERMS: COPOLYMER, POLYESTER, POLYETHER, POLYCARBONATE, POLYURETHANE.

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 5,019,467 (FUJIWARA) 28 May 1991, col. 3, lines 19 and 31-33.	1, 2, 9-12
Y	US, A, 5,223,353 (OHSAWA ET AL) 29 June 1993, col. 7, lines 49-63.	1, 2, 9-12
A	US, A, 5,061,581 (NARANG ET AL) 29 October 1991, col. 2, lines 50-61.	1-12
A	US, A, 3,967,978 (HONDA ET AL) 06 July 1976, abstract.	1-12
A,P	US, A, 5,407,593 (WHANG) 18 April 1995, col. 2, lines 31-33.	1-12

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

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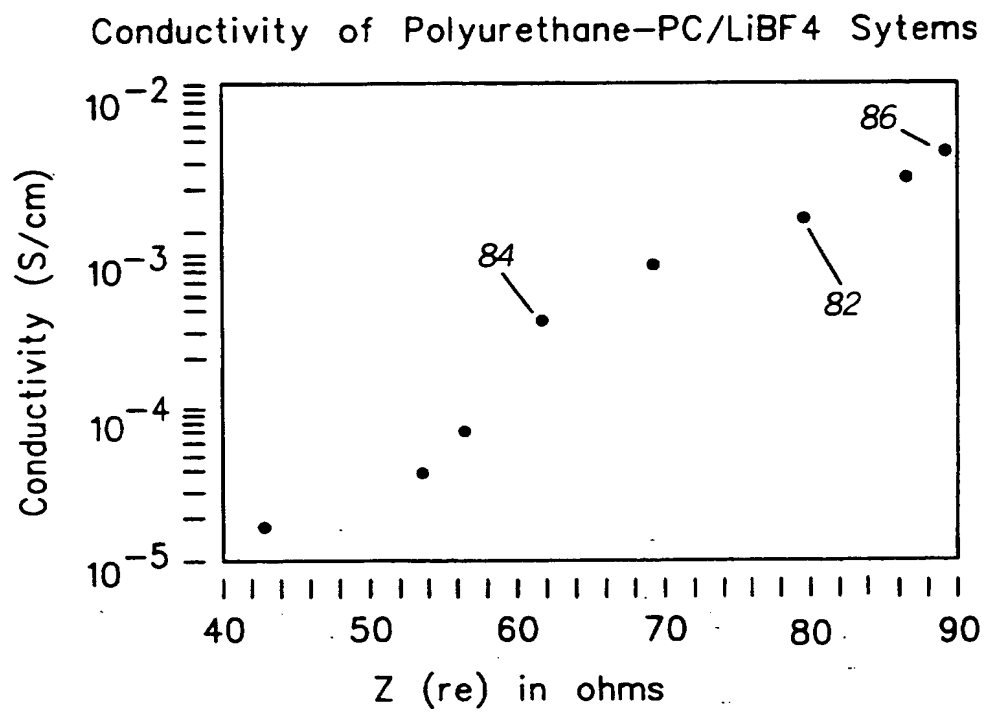
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*FIG. 5*



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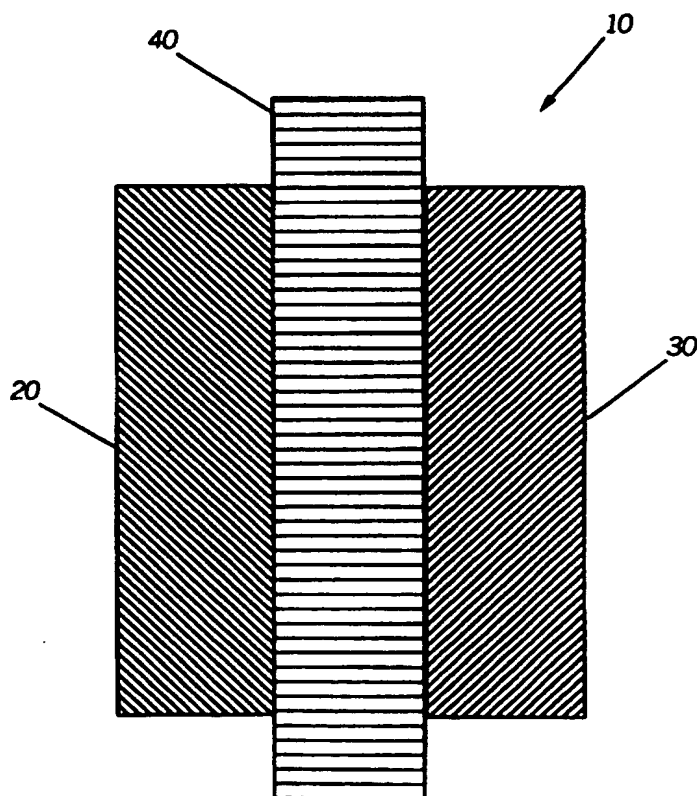
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(51) International Patent Classification <sup>6</sup> : <b>H01M 6/18, 10/40</b>		A1	(11) International Publication Number: <b>WO 96/03781</b>
			(43) International Publication Date: 8 February 1996 (08.02.96)
(21) International Application Number: PCT/US95/09117 (22) International Filing Date: 19 July 1995 (19.07.95) (30) Priority Data: 08/279,131          22 July 1994 (22.07.94)          US (71) Applicant (for all designated States except US): MOTOROLA INC. [US/US]; 1303 East Algonquin Road, Schaumburg, IL 60196 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): VENUGOPAL, Ganesh [IN/US]; 808 N.W. 89th Avenue, Plantation, FL 33324 (US). REICHERT, Veronica, R. [US/US]; Apartment 103, 4330 N. Reflections Boulevard, Sunrise, FL 33351 (US). ZHANG, Jinshan [CN/US]; 9146 N.W. 41st Manor, Coral Springs, FL 33065 (US). (74) Agents: MASSARONI, Kenneth, M. et al.; Motorola Inc., Intellectual Property Dept., 8000 West Sunrise Boulevard, Fort Lauderdale, FL 33322 (US).		(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG).  <b>Published</b> <i>With international search report.          Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	

(54) Title: POLYURETHANE BASED ELECTROLYTES FOR ELECTROCHEMICAL CELLS AND ELECTROCHEMICAL CELLS USING SAME

## (57) Abstract

An electrolyte system (40) for use in connection with an electrochemical cell (10). The cell (10) includes a positive (20) and a negative (30) electrode and the electrolyte system (40) disposed therebetween. The electrolyte system includes a liquid electrolyte adapted to provide ion transport between the positive and negative electrodes and a segmented block copolymeric support structure for engaging the liquid electrolyte.



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## POLYURETHANE BASED ELECTROLYTES FOR ELECTROCHEMICAL CELLS AND ELECTROCHEMICAL CELLS USING SAME

### Technical Field

5           This invention relates in general to electrolytes for electrochemical cells, and more particularly to polymer electrolytes for such cells.

### Background of the Invention

10           There has been a great deal of interest in developing better and more efficient methods for storing energy for applications such as radio communication, satellites, portable computers and electric vehicles to name but a few. There have also been concerted efforts to develop high energy, cost effective batteries having improved performance characteristics, particularly as compared to storage systems known in the art.

15           Rechargeable, or secondary cells are more desirable than primary (non-rechargeable) cells since the associated chemical reactions which take place at the positive and negative electrodes of the battery are reversible. Electrodes for secondary cells are capable of being regenerated (i.e. recharged) many times by the application of an electrical charge thereto. Numerous advanced electrode systems have been developed for storing electrical charge. Concurrently, much effort has been dedicated to the development of electrolytes capable of enhancing the capabilities of electrochemical cells.

25           Heretofore, electrolytes have been either liquid electrolytes as are found in conventional wet cell batteries, or solid films as are available in newer, more advanced battery systems. Each of these systems have inherent limitations, and related deficiencies which make them unsuitable for various applications.

30           Liquid electrolytes, while demonstrating acceptable ionic conductivity, tend to leak out of the cells into which they are sealed. While better manufacturing techniques have lessened the occurrence of leakage, cells still do leak potentially dangerous liquid electrolytes from time to time. This is particularly true of current lithium ion cells. Moreover, any leakage from the cell lessens the amount of electrolyte available in the cell,

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thus reducing the effectiveness of the cell. Cells using liquid electrolytes are also not available for all sizes and shapes of batteries.

Conversely, solid electrolytes are free from problems of leakage. However, they have inferior properties as compared to liquid electrolytes.

5 For example, conventional solid electrolytes have room temperature ionic conductivities in the range of  $10^{-5}$  S/cm, whereas acceptable ionic conductivity is  $> 10^{-3}$  S/cm. Good ionic conductivity is necessary to ensure a battery system capable of delivering usable amounts of power for a given application. Good conductivity is necessary for the high rate operation  
10 demanded by, for example, cellular telephones and satellites. Accordingly, solid electrolytes are not adequate for many high performance battery systems.

Examples of solid polymer electrolytes include dry solid polymer systems in which a polymer, such as polyurethane, is mixed with an  
15 electrolyte salt in dry or powdered form. These types of systems are disclosed in, for example, *Ionic Conductivity of Polyether-Polyurethane Networks Containing Alkali Metal Salts. An Analysis of the Concentration Effect*, Macromolecules, Vol. 17, No. 1, 1984, pgs. 63-66, to Killis, et al; and *Poly(dimethylsiloxane) - Poly(ethylene oxide) Based Polyurethane Networks Used As Electrolytes in Lithium Electrochemical Solid State Batteries*, Solid State Ionics, 15 (1985) 233-240, to Bouridah, et al.. Unfortunately, these dry systems, like the solid electrolytes discussed  
20 above, are characterized by relatively poor ionic conductivity.

One solution which has been proposed relates to the use of so-called  
25 gel electrolytes for electrochemical systems. Gels, or plasticized polymeric systems are wet systems, not dry, as described above. Heretofore most gel electrolyte systems have been based on homopolymers, i.e., single polymer systems. Homopolymer-based gel electrolytes have not been successful as they tend to dissolve in higher concentrations of the  
30 electrolyte solvent, thus losing mechanical integrity.

Accordingly, there exists a need for a new electrolyte system which combines the mechanical stability and freedom from leakage offered by solid electrolytes with the high ionic conductivities of liquid electrolytes.

### Brief Description of the Drawings

FIG. 1 is a schematic representation of an electrochemical cell in accordance with the instant invention;

FIG. 2 is a schematic morphology of unstretched segmented block polyurethane copolymers in accordance with the instant invention;

FIG. 3 is an AC impedance spectrum of a polyurethane/liquid electrolyte system in accordance with the instant invention;

FIG. 4 is a cyclic voltammagram of a polyurethane/liquid electrolyte blend; and

FIG. 5 is a chart illustrating the conductivity of solvent-cast polyurethane/liquid electrolyte blends as a function of electrolyte composition

### Detailed Description of the Preferred Embodiment

While the specification concludes with claims defining the features of the invention that are regarded as novel, it is believed that the invention will be better understood from a consideration of the following description in conjunction with the drawing figures, in which like reference numerals are carried forward.

Referring now to FIG. 1, there is illustrated therein a schematic representation of an electrochemical cell in accordance with the instant invention. The cell (10) includes a positive electrode (20) and a negative electrode (30). The positive electrode (20) may be fabricated of any of a number of chemical systems known to those of ordinary skill in the art. Examples of such systems include, but are not limited to, manganese oxide, nickel oxide, cobalt oxide, vanadium oxide, and combinations thereof. The negative electrode (30) may likewise be fabricated from any of a number of electrode materials known to those of ordinary skill in the art. Selection of the negative electrode material is dependent on the selection of the positive electrode so as to assure an electrochemical cell which will function properly for a given application. Accordingly, the negative electrode may be fabricated from, for example, alkali metals, alkali metal alloys, carbon, graphite, petroleum coke, and combinations thereof.

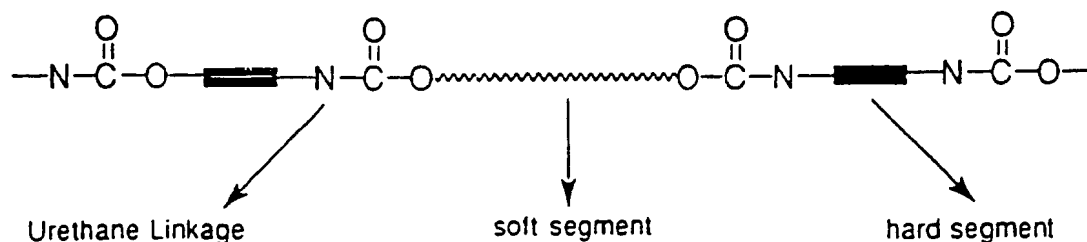
Operatively, disposed between the positive (20) and negative (30) electrodes is an electrolyte system (40). The electrolyte system (40) comprises an organic polymeric support structure adapted to engage, as

for example, by absorption, an electrochemically active species or material. The electrochemically active material may be a liquid electrolyte, such as a metal salt that is dissolved in an organic solvent and which is adapted to promote ion transport between said positive (20) and negative (30) electrodes.

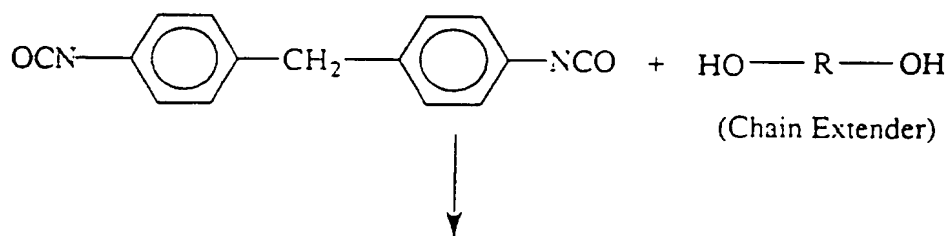
The liquid electrolyte absorbed by the organic support structure is selected to optimize performance of the positive (20) and negative (30) electrode couple. Therefore, in an embodiment for a lithium based electrochemical cell, the liquid electrolyte absorbed by the organic support structure is typically a solution of an alkali metal salt, or combination of salts, dissolved in an aprotic organic solvent or solvents. Typical alkali metal salts include, but are not limited to, salts having the formula  $M^+X^-$  where  $M^+$  is a alkali metal cation such as  $Li^+$ ,  $Na^+$ ,  $K^+$  and combinations thereof; and  $X^-$  is an anion such as  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $ClO_4^-$ ,  $BF_4^-$ ,  $PF_6^-$ ,  $AsF_6^-$ ,  $SbF_6^-$ ,  $CH_3CO_2^-$ ,  $CF_3SO_3^-$ ,  $(CF_3SO_2)_2N^-$ ,  $(CF_3SO_2)_3C^-$ , and combinations thereof. Aprotic organic solvents include, but are not limited to, propylene carbonate, ethylene carbonate, diethyl carbonate, dimethyl carbonate, dipropyl carbonate, dimethyl sulfoxide, acetonitrile, dimethoxyethane, diethoxyethane, tetrahydrofuran, and combinations thereof.

The organic polymeric support structure may be fabricated of a segmented block copolymer, that is a polymer that has at least two different blocks that form alternating segments along the polymer chain, each segment having different physical properties. An example of a segment block copolymer as used in the instant invention is the polyurethane thermoplastic elastomer which is a copolymer of a short-chain diisocyanate and a dihydroxy-terminated polyester (polyester diol). The condensation of these two species leads to the formation of a polymer having urethane linkages as illustrated in greater detail below.

The segmented block copolymer material from which the organic polymeric support structure is fabricated may be depicted as follows:



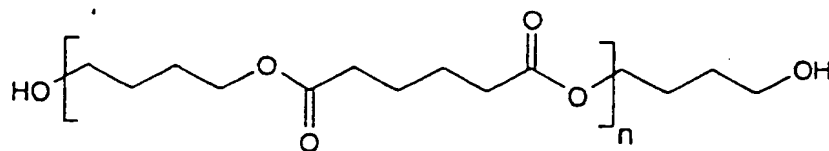
The short-chain diisocyanates provide the hard-rigid block segments of the copolymer. The short-chain diisocyanates are typically condensation products of diphenyl methane diisocyanate (MDI) and small molecule diols, for example, butane diol or ethylene glycol, or small molecule diamines such as 4-4'methylene bis (2-chloroaniline). The short-chain diols/diamines are also referred to as chain-extenders. The condensation reaction leading to the formation of the diisocyanate-terminated hard block segments may be described as follows:



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The long chain diols provide the soft block segment of the copolymer, and are typically relatively high-molecular weight (<3500 g/M) hydroxyl terminated polyesters or hydroxyl terminated polyethers. In one preferred embodiment the polyester is a polybutylene adipate (molecular weight approximately 2000 g/M). Alternatively, the polyester diols may be, for example, polyethylene adipate, polycaprolactone and combinations thereof. The long-chain diols forming the soft blocks typically appear as follows:

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polybutylene adipate

The hard block segments are known to aggregate through hydrogen bonding thus behaving as physical crosslinks for the soft block segments. As a result the polymeric material is an elastomer, that is, a rubbery material. Further, the hydrogen bonds responsible for aggregation of the

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hard blocks may be broken at high temperatures allowing the materials to behave as a thermoplastic. This property of the polyurethane offers an immense processing advantage since it may be processed into sheets and films using conventional polymer processing equipment, like those used for conventional thermoplastics, at high temperatures while behaving like elastomers at lower temperatures.

Referring now to FIG. 2, there is illustrated therein the schematic morphology of an unstretched segmented block polyurethane copolymer in accordance with the instant invention. The copolymer (60) is characterized by two general types of polymeric segments; a plurality of hard block segments (62, 64, and 66) which behave as physical crosslinks or backbone of the polymeric material. Disposed around and between the bodies of hard block segments are the long flexible chain polyester diols forming the soft block segment (68) of the copolymer material (60).

Exemplary materials which may be used as the segmented block copolymers for the organic polymeric support structure of the instant invention include a polyurethane, (either polyether or polyester based), polyester-polyether systems, polycarbonate-polyether systems and combinations thereof. Examples of segmented polyurethanes include Miles Laboratories Texin<sup>TM</sup> 460A, 455A, and 360D polyester/polyurethane material. These materials are approximately 2000 molecular weight alcohol terminated aliphatic polyesters, for example polyethylene or polybutylene adipates, condensed with a diisocyanate made from MDI and a chain extender, as discussed above. Other examples of polyester-polyurethanes include B.F. Goodrich's Estane<sup>TM</sup> 58206 and 58209, which are polyurethanes formed by the condensation of MDI-containing diisocyanates with alcohol terminated polyesters such as polyethylene and/or polybutylene adipates, polycaprolactone or polyesters containing aromatic moieties. Similar polyester based polyurethanes are also available from Dow Corporation under the name Pellethane<sup>TM</sup> 2355-75A and 2102-75A.

Heretofore, most blends of electrochemically active materials such as electrolytes and polymers other than polyurethane resulted in a significant deterioration of the mechanical properties of the polymer, usually forming tacky, viscous fluids. Further, prior art combinations of polymers with electrolytes resulted in electrolytic behavior considerably

lower than that considered acceptable in most electrochemical systems. Accordingly, an electrolyte in accordance with the instant invention has ionic conductivity as high as  $10^{-3}$  S/cm at room temperature, and has demonstrated excellent mechanical properties such as a shear modulus of approximately  $1 \times 10^5$  Pa at 30°C. Moreover, being elastomeric thermoplastics, these materials may form intimate contact with positive (20) and negative (30) electrodes.

More particularly, a polyurethane/liquid electrolyte system (40) in accordance with the instant invention may be mixed with cathode powders such as lithium manganese oxide, lithium nickel oxide or lithium cobalt oxide to form composite cathodes. Cathodes made in this fashion are essential for batteries which use polymer-based electrolytes since intimate contact between the active electrolyte material and the cathode cannot otherwise be achieved. It may further be appreciated that polyurethane liquid electrolyte blends in accordance with the instant invention may also be used to form composite anodes for batteries where lithium cannot be used.

The instant electrolyte system also has the important advantage of having a polymeric support structure which is easily processable and reprocessable, since the materials are thermoplastic elastomers. Other prior art gel systems are typically permanently chemically cross-linked either by radiation (e-beam, UV, etc.), or by using a chemical crosslinking agent, for example diisocyanates which can be used to cross-link polyether triols.

The following examples are intended to illustrate the advantages of the instant invention and they are not intended to be limitations thereon.

### EXAMPLE I

A polyurethane based electrolyte system in accordance with the instant invention was made by the solvent casting technique. 0.5 grams of Miles Texin 480A, polyester/polyurethane and 2.0g of a 1M solution of lithium tetrafluoroborate ( $\text{LiBF}_4$ ) solution in propylene carbonate were dissolved in approximately 8g of tetrahydrofuran (THF). This solution was poured into an aluminum dish and the THF was allowed to evaporate overnight yielding a film of the polyurethane based electrolyte. The

resulting electrolyte system was comprised of approximately 80 wt% of the liquid electrolyte (propylene carbonate/LiBF<sub>4</sub>).

Referring now to FIG. 3, there is illustrated therein the AC impedance spectrum of polyurethane blended with 80% (by weight) of 1M solution of lithium tetrafluoroborate and propylene carbonate as described above. The resistance of the film was approximately 55 Ohms. The thickness of the sample was approximately 0.075 cm with a cross-sectional area of approximately 1 cm<sup>2</sup>. Based upon this and as illustrated by the series of points shown in FIG. 3, the conductivity of the film was calculated to be approximately  $1.4 \times 10^{-3}$  S/cm.

## EXAMPLE II

A second polyurethane based electrolyte was made by the solvent casting technique as follows. 0.5 grams of a Miles Texin™ 480A polyester polyurethane and 0.8 grams of 1M solution of LiBF<sub>4</sub> solution in propylene carbonate (PC) were dissolved in about 8 grams of THF. The solution was poured in an aluminum dish and the THF was allowed to evaporate overnight yielding a film of the polyurethane based electrolyte. The resulting electrolyte comprised of 62 wt% of the liquid electrolyte (PC-LiBF<sub>4</sub>). Samples (approximately 1 cm<sup>2</sup> in area and 0.036 cm thick) for conductivity measurements were cut out from this solvent cast film. The resistance of the film was 130 Ohms and the conductivity was calculated to be  $3 \times 10^{-4}$  S/cm.

Referring now to FIG. 4, there is illustrated therein a cyclic voltammogram for the material obtained as described above. Data was collected at a scan rate of approximately 1 mV/s with platinum mesh working and counter electrodes, and a lithium reference electrode.

Cyclic voltammetry studies of the polyurethane electrolyte indicated that the material has good electrochemical stability in the voltage range between 0.2 and 4.2 V. The steep increase at around 4.2V indicates that the electrolyte is beginning to oxidize at this voltage. The source of the two peaks in the range 1 to 3.5V is not known and may be attributed to impurities in the polyurethane based electrolyte system. However, it is important to note that the current (y-axis) scale of these peaks is only in the microamp range and hence the concentration of the electrochemically active species involved is quite small.



## EXAMPLE III

A third polyurethane based electrolyte was made by the solvent casting technique as follows. 0.5 grams of Miles Texin™ 480A polyester polyurethane and 4.5 grams of 1M solution of LiBF<sub>4</sub> solution in propylene carbonate were dissolved in about 8 grams of THF. The solution was poured in an aluminum dish and the THF was allowed to evaporate overnight yielding a film of the polyurethane based electrolyte. The resulting electrolyte comprised 90 wt% of the liquid electrolyte (PC-LiBF<sub>4</sub>). Samples (approximately 1 cm<sup>2</sup> in area and 0.097 cm thick) for conductivity measurements were cut out from this solvent cast film. The resistance of the film was 47 ohms and the conductivity was calculated to be  $3 \times 10^{-3}$  S/cm.

## EXAMPLE IV

Polyurethane gels may also be made without the use of casting solvents like THF, as follows: Polyurethane films, approximately 0.058 cm in thickness, were made by compression molding at around 170°C in a Carver press. These films were then soaked in 1M solution of lithium tetrafluoroborate solution in propylene carbonate. After 48 hours the resulting polyurethane-liquid electrolyte blend contained about 63% of the liquid electrolyte. The sample thickness increased to 0.081 cm. Samples (approximately 1cm<sup>2</sup> in area) for conductivity measurements were cut out from this swollen film. The resistance of the film was 178 Ohms and the conductivity was calculated to be around  $4.5 \times 10^{-4}$  S/cm.

Referring now to FIG. 5, there is illustrated therein a chart demonstrating the conductivity of solvent cast/polyurethane liquid electrolyte blends as a function of liquid electrolyte composition. In this regard, the conductivity of Example I is illustrated at Point 82 while the conductivity of Examples II and III are illustrated by Points 84 and 86 respectively. As may be appreciated from a perusal of FIG. 5, numerous other samples having greater and lesser weight percents of liquid electrolyte in the solvent cast polyurethane material are illustrated. From this chart, one may conclude that with increasing wt% of the liquid electrolyte material, conductivity similarly increases. Limitations to increased conductivity are derived principally from decreasing mechanical stability of the polyurethane support structure with increased

concentrations of the liquid electrolyte. It is important to note, however, that wt% as high as those illustrated by Point 86 demonstrate quite acceptable conductivity while retaining excellent mechanical properties.

While the preferred embodiments of the invention have been  
5 illustrated and described, it will be clear that the invention is not so limited. Numerous modifications, changes, variations, substitutions and equivalents will occur to those skilled in the art without departing from the spirit and scope of the present invention as defined by the appended claims.

10 What is claimed is:

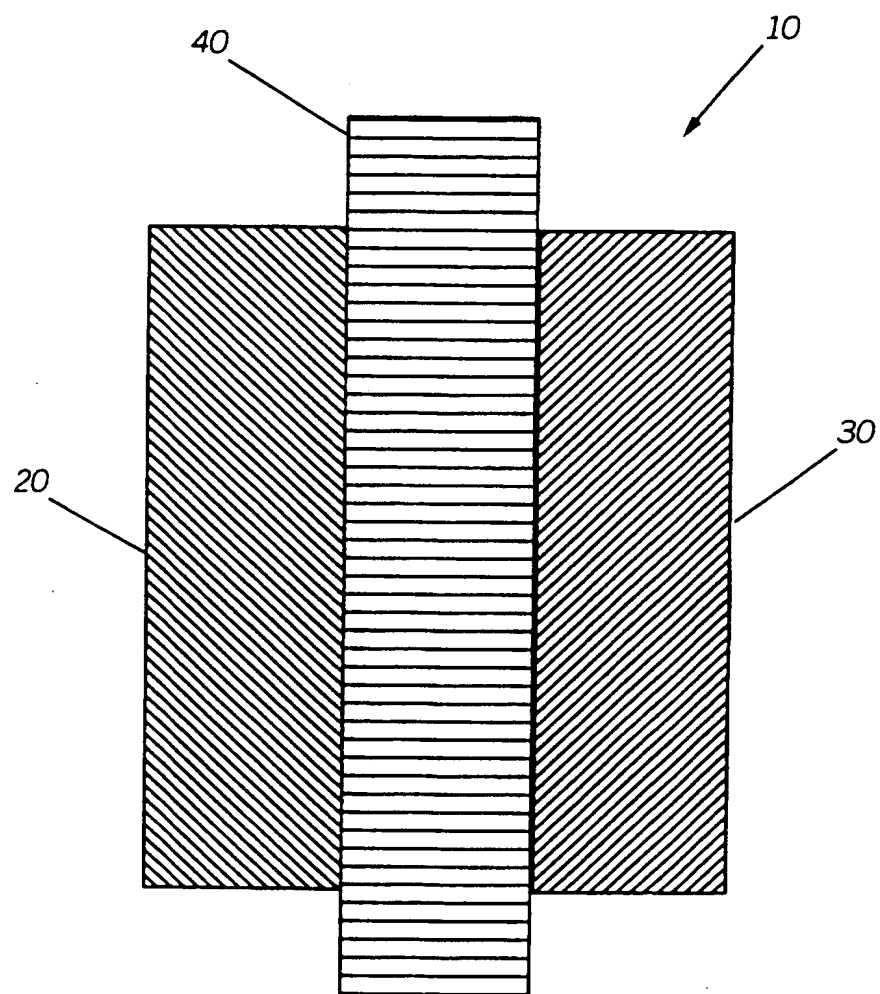
**Claims**

1. An electrolyte system for use in electrochemical cell having positive and negative electrodes, said electrolyte system comprising:  
an electrochemically active liquid electrolyte material adapted to  
5 promote ion transport between said positive and negative electrodes; and  
a polymeric support structure fabricated of a segmented block copolymeric material, said segmented block copolymeric material adapted to absorb said electrochemically active material.
- 10 2. An electrolyte system as in claim 1, wherein said polymeric support structure is a polyurethane-based polymeric support structure.
3. An electrolyte system as in claim 1, wherein said segmented  
15 block copolymeric material comprises first and second block segments.
4. An electrolyte system as in claim 3, wherein said first  
segmented block provides said electrolyte system with mechanical  
integrity.
- 20 5. An electrolyte system as in claim 3, wherein said first segmented block comprises short-chain diisocyanates.
6. An electrolyte system as in claim 3, wherein one of said  
segmented blocks is a soft block segment.
- 25 7. An electrolyte system as in claim 5, wherein said soft block segment is adapted to absorb said electrochemically active material.
8. An electrolyte system as in claim 7, wherein said soft-block  
segments are fabricated from hydroxyl terminated polyesters, hydroxyl  
30 terminated polyethers and combination thereof.
9. An electrolyte system as in claim 1, wherein said liquid  
electrolyte is a alkali metal salt dissolved in an aprotic organic solvent.

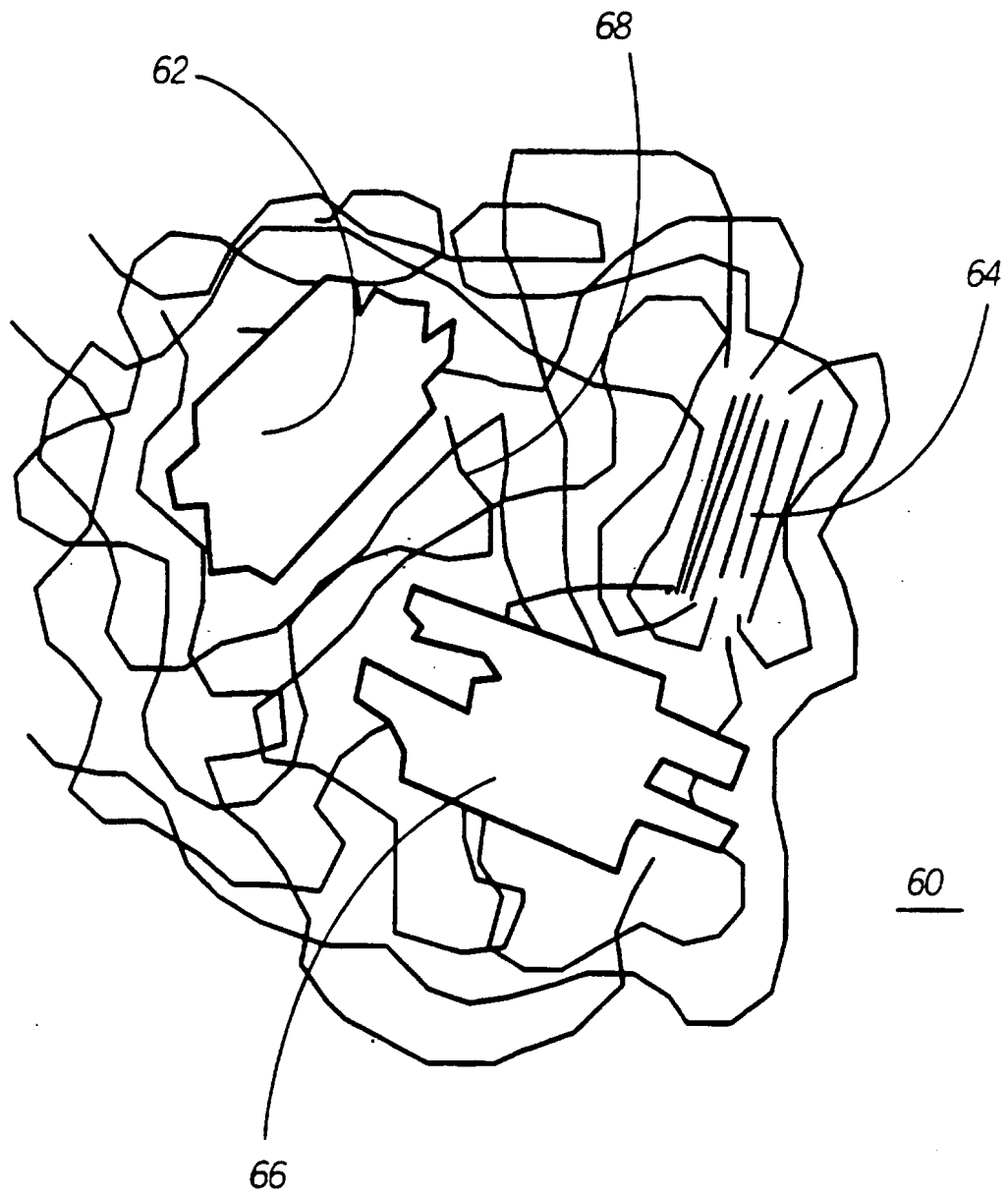
10. An electrolyte system as in claim 7, wherein alkali metal salt is selected from the group consisting of materials having the formula
- 5  $M^+X^-$  where:
- $M^+$  is an alkali metal cation such as  $Li^+$ ,  $Na^+$ , or  $K^+$ , and;  
 $X^-$  is an ion such as  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $ClO_4^-$ ,  $BF_4^-$ ,  $PF_5^-$ ,  $AsF_6^-$ ,  $SbF_6^-$ ,  $CH_3CO_2^-$ ,  $CF_3SO_3^-$ ,  $(CH_3CO_2)_2N^-$ ,  $(CF_3SO_2)_3C^-$ , and combinations thereof.
- 10
11. An electrolyte system as in claim 7, wherein said aprotic organic solvent is selected from the group consisting of propylene carbonate, ethylene carbonate, diethylcarbonate, dimethyl carbonate, dipropylcarbonate, dimethyl sulfoxide, acetonitrile, dimethoxyethane,
- 15 diethoxyethane, tetrahydrofuran and combinations thereof.
12. An electrolyte system as in claim 7 wherein said electrochemically active material is  $LiBF_4$  in propylene carbonate.

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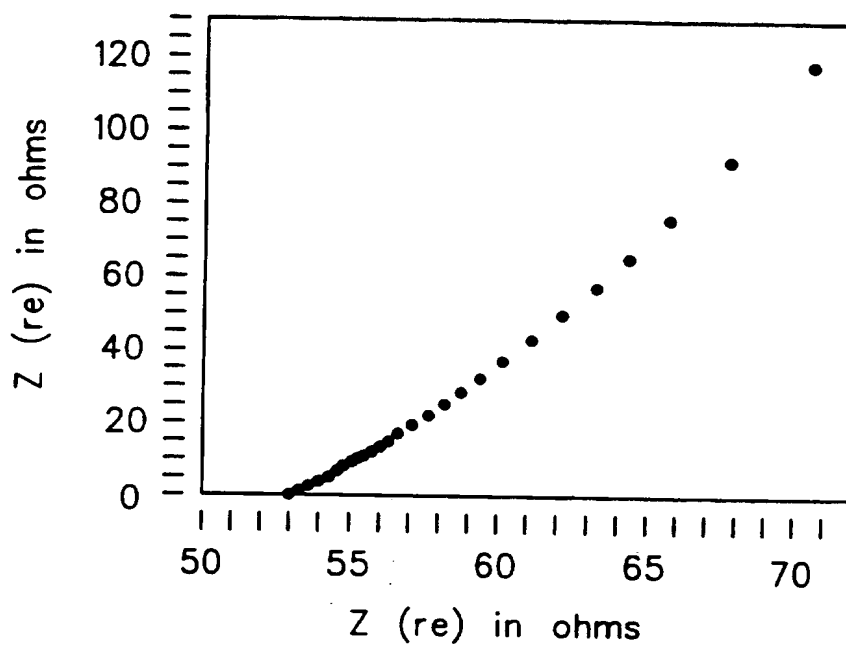
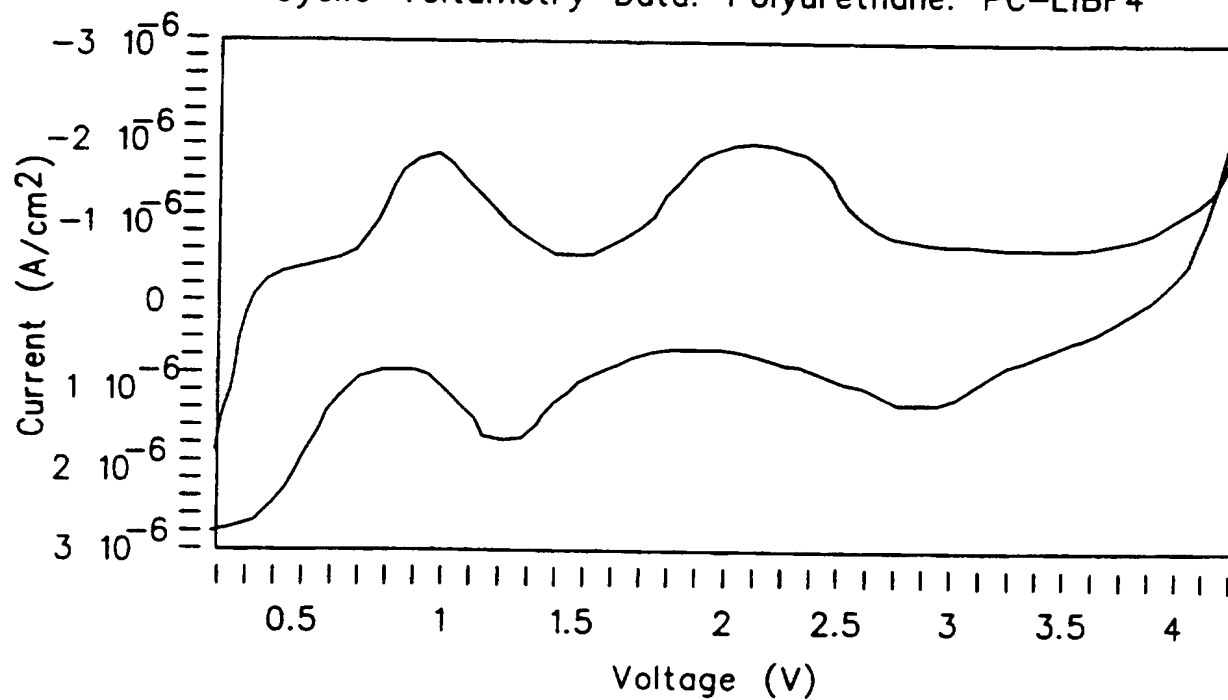
**FIG. 1**

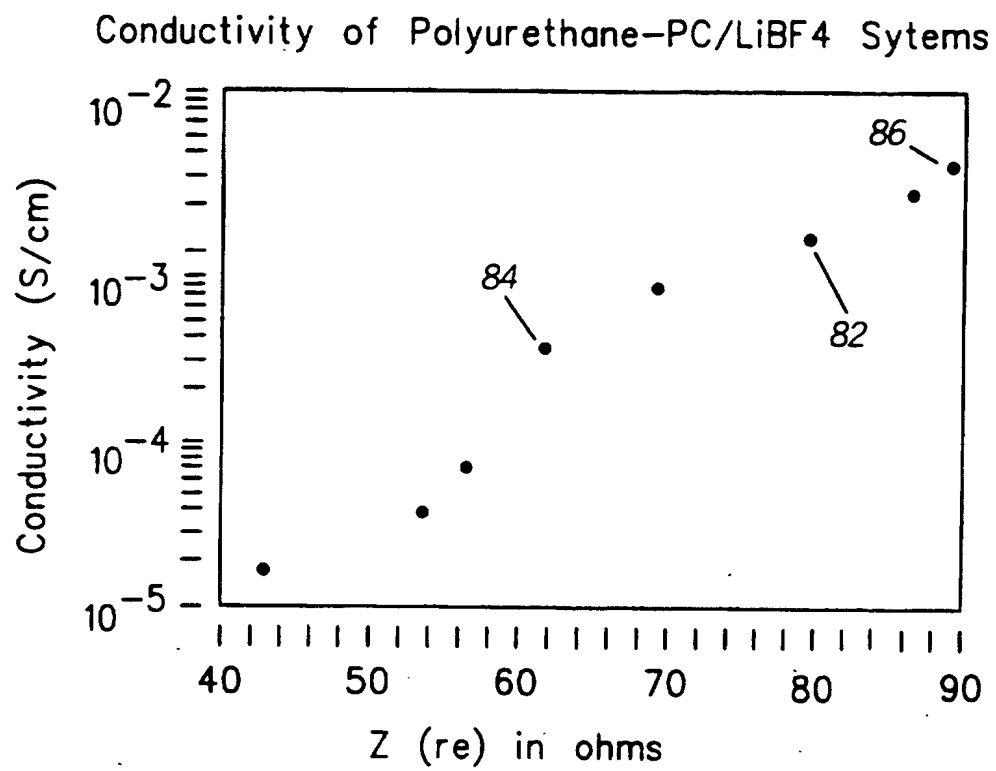


*FIG. 2*



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**FIG.3**POLYURETHANE; LiBF<sub>4</sub>-PC (1M) (20;80) (t=750 microns)**FIG.4**Cyclic Voltammetry Data: Polyurethane: PC-LiBF<sub>4</sub>

**FIG.5**



# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US95/09117

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : H01M 6/18, 10/40

US CL : 429/192; 252/62.2

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 429/188, 191, 192, 193; 252/62.2

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS: FILE USPAT

SEARCH TERMS: COPOLYMER, POLYESTER, POLYETHER, POLYCARBONATE, POLYURETHANE.

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 5,019,467 (FUJIWARA) 28 May 1991, col. 3, lines 19 and 31-33.	1, 2, 9-12
Y	US, A, 5,223,353 (OHSAWA ET AL) 29 June 1993, col. 7, lines 49-63.	1, 2, 9-12
A	US, A, 5,061,581 (NARANG ET AL) 29 October 1991, col. 2, lines 50-61.	1-12
A	US, A, 3,967,978 (HONDA ET AL) 06 July 1976, abstract.	1-12
A,P	US, A, 5,407,593 (WHANG) 18 April 1995, col. 2, lines 31-33.	1-12

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Further documents are listed in the continuation of Box C.

☐

See patent family annex.

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